



IN THE UNITED STATES PATENT OFFICE

.....
In re Appln. of: WHINNERY, Jr. et al.)

Serial Number: 10/652,647)

Examiner: COONEY, J.M.

Filed: 08/28/03)

Group Art Unit: 1711

For: **HIGH STRENGTH FOAM**)

TOOL AND METHOD)

Attorney Docket Number: SD-8466)
.....

DECLARATION UNDER C.F.R. §1.132

Sir:

I, Dr. LeRoy L. Whinnery, Jr., currently of 190 Blackstone Drive, Danville, CA 94506, do declare and state as follows:

That I received a Bachelor of Science degree in Chemistry from Ithaca College in 1985 and that I received a Doctor of Philosophy degree from the California Institute of Technology in 1990 under the direction of John E. Bercaw, Ph.D., Centennial Professor of Chemistry;

That my graduate dissertation focused on the mechanistic and synthetic organometallic chemistry; and

That I have been employed by Sandia National Laboratories in Livermore, California, since 1990 working in a number of diverse projects, particularly, in materials research of polymer foam.

In the matter of U.S. Patent Application Serial Number 10/652,647 of LeRoy Whinnery, Jr., Steven Goods, Craig Henderson, and Thomas Bennett, filed on 08/28/2003, entitled "HIGH STRENGTH FOAM TOOL AND METHOD" (the "present invention"), the following observations and data were obtained while preparing and testing sample foam parts made using the foam formulation recited by Hayash, Jr. et al., U.S. Patent Serial Number

3,673,128 (hereinafter “Hayash”) in order compare the Hayash structure with that provided by the claims of the present invention.

Declarant, therefore, states that it was found that a one-to-one correspondence between Hayash and the present invention was not possible due to processing limitations with both formulations. In particular, the Hayash polymer gel as described in its written description a final product having a density of about 2 lb/ft³ which was far lower than the target density of the present invention (about 35 lb/ft³ – 48 lb/ft³). Furthermore, the Hayash formulation was found to be too viscous and to allow for incorporating a bulk filler within the mixed resins as is used in the present invention to prevent the formation of density gradients within the gelling polymer. It, therefore, was found to be necessary to modify the Hayash formulation by eliminating the blowing agent to increase its density. **TABLE 1**, below, shows the formulations used to prepare initial trial samples of the Hayash foam prepared without the blowing agent in order to increase the density of this material to a density approximating the density of the present invention.

In addition to eliminating the blowing agent, it was also necessary to reduce the catalyst content in order to slow the polymerization process to a point where the materials could be handled. Formulation #1 was prepared using the ratios of the constituent ingredient materials recited by the Hayash et al., but, as noted, the reaction of this mixture proceeded far too quickly to be handled properly: setting up almost immediately (see **FIGURE 1**). Formulation #2 was prepared using about ¼ of the quantity of catalyst used in formulation #1 but this material behaved much as did formulation #1, again reacting too rapidly to be handled. Formulation #3 was prepared using only about ¼ of the quantity of catalyst used in formulation #2, or about ⅓ of that used in formulation #1 and was found to react slowly enough to allow mixing and casting a “slug,” or block, of foam from which a density measurement could be made. While no attempt was made to achieve any particular target density, sample prepared with formulation #3 was found to exhibit a density of about 52 lb/ft³.

TABLE 1

Formulation Ingredients	#1 (gms.)	#2 (gms.)	#3 (gms.)
EPON [®] 154 ¹	101.0	100.9	100.0
PAPI [®] 27 ²	94.6	94.2	94.1
DABCO DC 197 ³	4.0	4.0	4.0
DABCO 33-LV ⁴	6.0	1.55	0.4
CFC-113 ⁵	---	---	---

1. Epoxy resin, epoxy equivalent weight 178

2. Polymethylene polyphenyl isocyanate, isocyanate equivalent weight 131

3. Poly(siloxane-glycol) surfactant

4. Tertiary amine catalyst - 33% triethylenediamine / 67% dipropylene glycol

5. Blowing agent - 1,1,2-trichloro-1,2,2-trifluoroethane

Test specimen consisting of cylinders 0.78 inches in diameter by 1 inch in length were cut from the block of Hayash foam material prepared using formulation #3. Three samples were then subjected to a standard room temperature, mechanical compression test at a stain rate of about 2×10^{-4} in/sec. A representative example of the recorded compression test response for Hayash formulation #3 at room temperature is provided in **FIGURE 2** and shows a yield stress of 42 MPa and a maximum stress at fracture of 61 MPa.

Similar test specimens were prepared from the formulation of the present invention as shown in **TABLE 2**. The test specimen again consisted of cylinders 0.78 inches in diameter by 1 inch in length. The density of this material, however, was slightly less than the Hayash material: about 47 lb/ft³. Moreover, a bulk filler in the form of glass micro-balloons was incorporated into the mixture in order to prevent the formation of a density gradient through the thickness of the cast foam block. A representative example of the recorded room temperature compression test response of the present invention formulation is shown in **FIGURE 3** and shows a yield stress of 64 MPa and a maximum stress at fracture of 79 MPa.

TABLE 2

Formulation Ingredients	TEPIC 1 (gms.)
EPON [®] 826 ¹	3655
PAPI [®] 2094 ²	6833
GMB ³	1840
DC 193 ⁴	458
TMR 30 ⁵	38.4
POLYCAT 8 ⁶	17.5

1. Epoxy resin, epoxy equivalent weight 178 – 186

2. Polymethylene polyphenyl isocyanate, isocyanate equivalent weight 131.5

3. Glass microballoons

4. Poly(siloxane-glycol) surfactant

5. Tertiary amine catalyst - 2,4,6-tris(dimethylaminomethyl)phenol

6. Cyclic amine - N,N-Dimethylcyclohexylamine

As can be seen in **FIGURES 2** and **3** the room temperature compression test results show the material of the present invention to exhibit peak strength about 130% greater and a yield strength about 150% greater than the Hayash material despite the fact that the density of material of the present invention was about 10% less than that of the Hayash material. It should be noted herein that the presence of the bulk filler was found to affect the strength of the final polymerized material only with respect to its effect on the density of the material. In particular, the addition of the filler was used to lower the density of the cast material and thereby lower its overall strength as is shown in **FIGURE 4**.

However, while the room temperature performance is illustrative, it is of particular interest to compare the high temperature compression strength of the Hayash foam material with that of the present invention. This is because the material of the present invention is designed to function as a high temperature lay-up tool capable of sustained and repeated use at temperature of 200°C.

Declarant states that it was discovered that the material of the present invention could be processed through a high temperature (200°C) post-cure stage following a normal 65°C

cure cycle and still maintain most of its room temperature compression strength. This particular feature allows this material to be used as a mold for composite lay-up manufacture because the epoxy impregnated carbon “cloth” composite must be cured at temperature up to 200°C.

TABLE 3

<i>HIGH TEMPERATURE POST-CURING PROCESS</i>	
Step 1	<i>returning the foam part to the 65°C oven for 2 hours;</i>
Step 2	<i>ramping the temperature of the oven up to 150°C over 8 hours and hold at this temperature for an additional 5 hours;</i>
Step 3	<i>ramping the temperature of the oven up to 180°C over 8 hours and hold at this temperature for an additional 5 hours;</i>
Step 4	<i>ramping the temperature of the oven up to 200°C over 5 hours and hold at this temperature for an additional 5 hours; and</i>
Step 5	<i>ramping the temperature of the oven down to 65°C over 5 hours and hold at this temperature for an additional 1 hour.</i>

Declarant states that the block of foam prepared using formulation #3, shown in **TABLE 1**, was subjected to the post-processing steps shown above in **TABLE 3**. From this block of foam, three test samples were cut and tested at 200°C. The samples again consisted of cylinders 0.78 inches in diameter by 1 inch in length. Two samples were then subjected to a mechanical compression test again at a strain rate of about 2×10^{-4} in/sec, while maintaining the sample at a temperature of 200°C. The density of this material was about 52 lb/ft³. A representative example of the recorded compression test response for Hayash formulation #3 at 200°C is provided in **FIGURE 5** and shows an average yield stress of 17 MPa and an average maximum stress at fracture of 28 MPa.

Similar test specimens were prepared from the formulation of the present invention, again as shown in **TABLE 2**. Representative samples are shown in **FIGURE 6**. The test specimen again consisted of cylinders 0.78 inches in diameter by 1 inch in length. The density of these samples was about 47 lb/ft³. A representative example of the recorded room

temperature compression test response of the present invention formulation is shown in **FIGURE 7** and shows a yield stress of 43 MPa and a maximum stress at fracture of 54 MPa.

As can be seen in **FIGURES 5** and **7** the results of the high temperature compression test taken at 200°C show the material of the present invention to exhibit an peak strength that is nearly 200% greater and a yield strength over 250% greater than the Hayash material, again despite the fact that the density of material of the present invention was about 10% less than that of the Hayash material.

Declarant further states that 3 additional blocks of a lower density foam prepared using the Hayash formulation shown below in **TABLE 4**, were subjected to the post-processing steps shown above in **TABLE 3**. These samples exhibited a density of about 15 lb/ft³.

TABLE 4

Formulation Ingredients	#4a (gms.)	#4b (gms.)	#4c (gms.)
EPON [®] 154	101.0	100.9	100.0
PAPI [®] 27	94.6	94.2	94.1
DABCO DC 197	4.0	4.0	4.0
DABCO 33-LV	6.0	1.55	0.4
CFC-113 ¹	6.9	7.1	6.9

1. Blowing agent – 1,1,2-trichloro-1,2,2-trifluoroethane

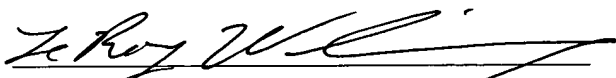
Each of the three new Hayash foam blocks performed poorly when subjected to the post-processing steps of **TABLE 3**. As shown in **FIGURES 8A – 8C**, and **9A** and **9B** the temperature excursion used to post-cure this material appears to have initiated an exothermic reaction within the material. Each block of foam thus prepared was heard “popping” during the heating steps. After processing, each was found to be cracked and showed evidence of moderate to severe charring at its core. This behavior is dramatically apparent in foam block #4b shown in cross section in **FIGURE 9B**. However, even the less severely affected foam

blocks, #4a and #4c, cracked (see **FIGURE 8B**) and charred (see **FIGURE 8C**) after thermal processing.

In conclusion, Declarant states that the test data presented above demonstrates the following:

- (1) That polymer foams prepared using the materials formulation recited by Hayash et al., could not be prepared in the density range of the present invention without eliminating the use of the blowing agent and reducing the proportion of catalyst used;
- (2) That higher density foams prepared using the modified Hayash formulation exhibited room temperature yield and peak fracture strengths about 30% less than those exhibited by foams prepared by the formulation of the present invention;
- (3) That higher density foams prepared using the modified Hayash et al., formulation and thermally post-cured, as recited by the present invention, exhibited an average yield stress of and an average peak fracture stress of only about one-half that exhibited by the foams prepared by the formulation of the present invention;
- (4) That lower density foams prepared using the modified Hayash formulation and thermally post-cured, as recited by the present invention, exhibited significant damage caused by charring and cracking and rendering them unusable; and
- (5) That foams prepared using formulation of the present invention and thermally post-cured, as recited by the present invention, exhibited no evidence of either charring or cracking.

Further the Declarant states not.


Declarant: LeRoy L. Whinnery, Jr.

Signed at Livermore, California, this 1st day of February, 2007.